

This Page Is Inserted by IFW Operations
and is not a part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

As rescanning documents *will not* correct images,
please do not report the images to the
Image Problem Mailbox.

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



B38

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : G02F 1/133, B41J 2/01, B29C 67/00, G09F 9/00, G04B 47/00, G09F 9/37		A1	(11) International Publication Number: WO 98/03896
			(43) International Publication Date: 29 January 1998 (29.01.98)
(21) International Application Number: PCT/US96/13469			(81) Designated States: AL, AM, AT, AU, AZ, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).
(22) International Filing Date: 20 August 1996 (20.08.96)			
(30) Priority Data: 60/022,222 19 July 1996 (19.07.96) US			
(60) Parent Application or Grant (63) Related by Continuation US 60/022,222 (CIP) Filed on 19 July 1996 (19.07.96)			
(71)(72) Applicant and Inventor: JACOBSON, Joseph, M. [US/US]; Apartment 1, 31 Linnaean Street, Cambridge, MA 02138 (US).			
(74) Agents: SMITH, James, M. et al.; Hamilton, Brook, Smith & Reynolds, Two Militia Drive, Lexington, MA 02173 (US).			
(54) Title: ELECTRONICALLY ADDRESSABLE MICROENCAPSULATED INK AND DISPLAY THEREOF			
(57) Abstract <p>We describe a system of electronically active inks which may include electronically addressable contrast media, conductors, insulators, resistors, semiconductive materials, magnetic materials or spin materials. We further describe a printing system capable of laying down said materials in a definite pattern. Such a system may be used for instance to print a flat panel display complete with onboard drive logic or to print a working logic circuit onto any of a large class of substrates.</p>			

-1-

ELECTRONICALLY ADDRESSABLE MICROENCAPSULATED INK
AND DISPLAY THEREOF

Related Applications

This application claims priority to U.S. Provisional
5 Application Serial No. 60/022,222, filed July 19, 1996 the
contents of which are incorporated herein by reference in
their entirety.

Background

Currently printing of conductors and resistors is
10 well known in the art of circuit board manufacture. In
order to incorporate logic elements the standard practice
is to surface mount semiconductor chips onto said circuit
board. To date there does not exist a system for directly
printing said logic elements onto an arbitrary substrate.

15 In the area of flat panel display drivers there
exists technology for laying down logic elements onto
glass by means of vacuum depositing silicon or other
semiconductive material and subsequently etching circuits
and logic elements. Such a technology is not amenable to
20 laying down logic elements onto arbitrary surface due to
the presence of the vacuum requirement and the etch step.

In the area of electronically addressable contrast
media as may be used to effect a flat panel display
emissive and reflective electronically active films such
25 as electroluminescent and electrochromic films, polymer
dispersed liquid crystal films, and bichromal microsphere
elastomeric slabs are known. No such directly
electronically addressable contrast media however is
amenable to printing onto an arbitrary surface.

-2-

Finally in the area of surface actuators electrostatic motors which may be etched or non-etched are known in the art. In the first case such etched devices suffer from their inability to be fabricated on arbitrary
5 surfaces. In the second case, non-etched devices suffer from the inability to incorporate drive logic and electronic control directly onto the actuating surface.

It is an object of the present disclosure to overcome the limitations of the prior art in the area of printable
10 logic, display and actuation.

Summary of the Invention

In general the present invention provides a system of electronically active inks and means for printing said inks in an arbitrary pattern onto a large class of
15 substrates without the requirements of standard vacuum processing or etching. Said inks may incorporate mechanical, electrical or other properties and may provide but are not limited to the following function: conducting, insulating, resistive, magnetic, semiconductive, light
20 modulating, piezoelectric, spin, optoelectronic or thermoelectric.

In one embodiment this invention provides for a microencapsulated electric field actuated contrast ink system suitable for addressing by means of top and bottom
25 electrodes or solely bottom electrodes and which operates by means of a bichromal dipolar microsphere, electrophoretic, dye system, liquid crystal, electroluminescent dye system or dielectrophoretic effect. Such an ink system may be useful in fabricating an
30 electronically addressable display on any of a large class of substrate materials which may be thin, flexible and may result in an inexpensive display.

-3-

In another embodiment this invention provides for a semiconductive ink system in which a semiconductor material is deployed in a binder such that when said binder is cured a percolated structure with semiconductive properties results.

In another embodiment this invention provides for systems capable of printing an arbitrary pattern of metal or semiconductive materials by means of photoreduction of a salt, electron beam reduction of a salt, jet electroplating, dual jet electroless plating or inert gas or local vacuum thermal, sputtering or electron beam deposition.

In another embodiment this invention provides for semiconductor logic elements and electro-optical elements which may include diode, transistor, light emitting, light sensing or solar cell elements which are fabricated by means of a printing process or which employ an electronically active ink system as described in the aforementioned embodiments. Additionally said elements may be multilayered and may form multilayer logic including vias and three dimensional interconnects.

In another embodiment this invention provides for an electronically addressable display in which some or all of address lines, electronically addressable contrast media, logic or power are fabricated by means of a printing process or which employ an electronically active ink system as described in the aforementioned embodiments.

In another embodiment this invention provides for an electrostatic actuator or motor which may be in the form of a clock or watch in which some or all of address lines, logic or power are fabricated by means of a printing process or which employ an electronically active ink system as described in the aforementioned embodiments.

-4-

In another embodiment this invention provides for a wrist watch band which includes an electronically addressable display in which some or all of address lines, electronically addressable contrast media, logic or power are fabricated by means of a printing process or which employ an electronically active ink system as described in the aforementioned embodiments.

In another embodiment this invention provides for a spin computer in which some or all of address lines, electronically addressable spin media, logic or power are fabricated by means of a printing process or which employ an electronically active ink system as described in the aforementioned embodiments.

Further features and aspects will become apparent from the following description and from the claims.

Brief Description of the Drawings

The foregoing and other objects, features and advantages of the invention will be apparent from the following more particular description of preferred embodiments of the invention, as illustrated in the accompanying drawings in which like reference characters refer to the same parts throughout the different views. The drawings are not necessarily to scale, emphasis instead being placed upon illustrating the principles of the invention.

Figures 1A-F are schematic representations of means of fabricating particles with a permanent dipole moment.

Figures 2A-C are schematic representations of means of microencapsulation.

Figures 3A-E are schematic representations of microencapsulated electronically addressable contrast media systems suitable for top to bottom addressing.

-5-

Figure 4A-M are schematic representations of microencapsulated electronically addressable contrast media systems suitable for bottom addressing.

Figures 5A-D are schematic representations of microencapsulated electronically addressable contrast media systems based on a dielectrophoretic effect.

Figures 6A-B are schematic representations of microencapsulated electronically addressable contrast media systems based on a frequency dependent dielectrophoretic effect.

Figures 6C-E are plots of the dielectric parameter as a function of frequency for various physical systems.

Figures 7A-D are schematic representations of electronic ink systems and means for printing the same.

Figure 8 is a schematic representation of a laser reduced metal salt ink system.

Figures 9A-E are schematic representations of electronic ink systems and means for printing the same.

Figures 10A-D are schematic diagrams of printed transistor structures.

Figure 11 is a schematic diagram of an electronic display employing printed elements.

Figure 12 is a schematic diagram of an electrostatic motor which may be in the form of a watch or clock in which said electrostatic elements are printed

Figure 13 is a schematic diagram of a watch in which the wristband of said watch incorporates an electronically addressable display having printed elements.

Figure 14 is a schematic diagram of a spin computer.

30 Detailed Description of a Preferred Embodiment

Means are known in the prior art for producing

-6-

bichromal particles or microspheres for use in electronic displays. Such techniques produce a particle that does not have an implanted dipole moment but rather relies in general on the Zeta potential of the material to create a permanent dipole. Such a scheme suffers from the fact that it links the material properties to the electronic properties thus limiting the size of the dipole moment which may be created. Figure 1 details means of producing particles, either bichromal as might be used in an electrostatic display, or monochromal as might be used in a dielectrophoretic display, with an implanted dipole moment.

Referring to Figure 1 A atomizing nozzles 1 are loaded with materials 12 and 13 which may be differentially colored. A first atomizing nozzle may be held at a positive potential 3 and a second nozzle may be held at a negative potential 4. Such potentials aid in atomization and impart a charge to droplets which form from said nozzles producing positively charge droplets 5 and negatively charged droplets 6. Such opposite charged droplets are attracted to each other electrostatically forming an overall neutral pair. After the formation of a neutral particle there is no more electrostatic attraction and no additional droplets are attracted to the neutral pair. If said material 12 and 13 are such that they are liquid when exiting said nozzles and either cool to form a solid or undergo a chemical reaction which may involve an additional hardening agent to form a solid then said charge may be trapped on each side of said neutral pair forming a bichromal solid particle with an implanted dipole 16. By suitable choice of materials such as polyethylene, polyvinylidene fluoride or other materials such metastable dipoles may persist for long periods of

-7-

time as is known in the art of electrets. A heating element 7 may serve to reheat said pair thus minimizing surface tension energy and serving to reform said pair into a more perfect spherical shape. Finally a set of electrodes 8 biased at either the same or opposite voltage may be employed to trap particles which are not overall charge neutral.

Referring to Figure 1B a similar apparatus may be employed to create a monochromal particle with an implanted dipole. In this arrangement nozzles containing material of the same color 12 are employed as before to create a monochromal particle with implanted dipole 21.

Referring to Figure 1C and E alternative means are shown for producing a bichromal particle with implanted dipole by means of combining two differentially colored materials 12 and 13 on a spinning disk 11 or in a double barreled nozzle 19. Said materials are charged by means of positive electrode 14 and negative electrode 15 and combine by means of electrostatic attraction at the rim of said disk or exit of said double barrel nozzle to form bichromal particle with implanted dipole moment 16. Said means differs from that known in the art by means of causing said two different materials 12 and 13 to coalesce by means of electrostatic attraction as opposed to relying on surface properties and interactions between the two materials. Additionally the present scheme creates a particle with an implanted dipole moment 16 which may serve to create a large dipole moment than that possible from the naturally occurring Zeta potential.

Referring to Figure 1D and F a similar apparatus may be employed to create a monochromal particle with an implanted dipole. In this arrangement nozzles containing material of the same color 12 are employed as before to

- 8 -

create a monochromal particle with implanted dipole 21.

A large number of techniques are known in the literature for microencapsulating one material inside of another material. Such techniques are generally used in the paper or pharmaceutical industry and do not generally produce a microcapsule which embodies simultaneously the properties of optical clarity, high dielectric strength, impermeability and resistance to pressure. With proper modification however these techniques may be made amenable to microencapsulating systems with electronic properties.

Referring to Figure 2A an internal phase 25 which may be a liquid or may be a solid with an additional associated surface layer 27. Said internal phase if liquid or said associated surface layer may contain a polymer building block, such as Adipoyl Chloride in Silicone Oil. Said internal phase, with associated boundary layer in the case of a liquid, may then be dispersed in a continuous phase liquid 30 which may be an aqueous solution which is immiscible with said internal phase or associated surface layer. Finally a solution 40 may be added which contains another polymer building block or cross linking agent may be added to continuous phase liquid 30. Said solution 40 has the effect of forming a solid layer at the interface of the internal phase or associated surface layer and said continuous phase liquid 30 thus acting to microencapsulate said internal phase.

Referring to Figure 2B an internal phase 25 which may be a solid or a liquid may be caused to pass through a series of liquid films 50, 60, 70 which may contain polymer building blocks, cross linking agents and overcoat materials such that a final microcapsule 120 results comprised of an internal phase 25, an associated surface layer 27 and an outer shell 80.

-9-

An alternate means of microencapsulation is shown in Figure 2C. In this scheme a light source 82 which may be a UV light source passes in some areas through a photomask 84 exposing a crosslinkable polymer which may be caused to
5 form a cellular structure 86. The individual cells of said cellular structure may then be filled with an internal phase 25.

Employing the systems described in Figures 2A-C it is possible to microencapsulate systems with electronically
10 active properties specifically electronically addressable contrast media. Figure 3 details such electronically addressable contrast media systems which are suitable for addressing by means of a top clear electrode 100 and bottom electrode 110. Referring to Figure 3A a
15 microcapsule 120 may contain a microsphere with a positively charged hemisphere 142 and a negatively charged 140 hemisphere and an associated surface layer material 130. If said hemispheres are differentially colored an electric field applied to said electrodes may act to
20 change the orientation of said sphere thus causing a perceived change in color.

Referring to Figure 3B a microcapsule 120 may contain positively charged particles of one color 210 and negatively charged particles of another color 220 such
25 that application of an electric field to said electrodes causes a migration of the one color or the other color, depending on the polarity of the field, toward the surface of said microcapsule and thus effecting a perceived color change. Such a system constitutes a microencapsulated
30 electrophoretic system.

Referring to Figures 3C-D a microcapsule 120 may contain a dye, dye precursor or dye indicator material of a given charge polarity 230 or a dye, dye precursor or dye

-10-

indicator material attached to a particle of given charge polarity such as a microsphere with an appropriate surface group attached and a reducing, oxidizing, proton donating, proton absorbing or solvent agent of the other charge polarity 240 or a reducing, oxidizing, proton donating, proton absorbing or solvent agent attached to a particle of the other charge polarity. Under application of an electric field said dye substance 230 is maintained distal to said a reducing, oxidizing, proton donating, proton absorbing or solvent agent 240 thus effecting one color state as in Figure 3C. Upon deapplication of said electric field said dye substance and said a reducing, oxidizing, proton donating, proton absorbing or solvent agent may bond to form a complex 245 of second color state. Suitable materials for use in this system are leuco and lactone dye systems and other ring structures which may go from a state of one color to a state of a second color upon application of a reducing, oxidizing or solvent agent or dye indicator systems which may go from a state of one color to a state of a second color upon application of a proton donating or proton absorbing agent as is known in the art. An additional gel or polymer material may be added to the contents of said microcapsule in order to effect a bistability of the system such that said constituents are relatively immobile except on application of an electric field.

Referring to Figure 3E a microcapsule 120 may contain phosphor particle 255 and photoconductive semiconductor particles and dye indicator particles 260 in a suitable binder 250. Applying an AC electric field to electrodes 100 and 110 causes AC electroluminescence which causes free charge to be generated in the semiconducting material further causing said dye indicator to change color state.

-11-

Referring to Figures 4A-M it may be desirable to develop ink systems which are suitable for use without a top transparent electrode 100 which may degrade the optical characteristics of the device. Referring to
5 Figures 4A and B the chemistry as described in reference to Figures 3C-D may be employed with in-plane electrodes such that said chemistry undergoes a color switch from one color state to a second color state upon application of an electric field to in-plane electrodes 270 and 280. Such a
10 system is viewed from above and thus said electrodes may be opaque and do not effect the optical characteristics of said display.

As another system in-plane switching techniques have been employed in transmissive LCD displays for another
15 purpose, namely to increase viewing angle of such displays. Referring to Figures 4C and 4D a bistable liquid crystal system of the type demonstrated by Hatano et. al. of Minolta Corp. is modified to be effected by in plane electrodes such that a liquid crystal mixture
20 transforms from a first transparent planar structure 290 to a second scattering focal conic structure 292.

Referring to Figure 4E the system of Figure 3E may be switched by use of in-plane electrodes 270 and 280.

Other systems may be created which cause a first
25 color change by means of applying an AC field and a second color change by means of application of either a DC field or an AC field of another frequency. Referring to Figures 4F-G a hairpin shaped molecule or spring in the closed state 284 may have attached to it a positively charged 282
30 and a negatively charged 283 head which may be microspheres with implanted dipoles. Additionally one side of said hairpin shaped molecule or spring has attached to it a leuco dye 286 and the other side of said

-12-

hairpin shaped molecule or spring has attached to it a reducing agent 285. When said molecule or spring is in the closed state 284 then said leuco dye 286 and said reducing agent 285 are brought into proximity such that a bond is formed 287 and said leuco dye is effectively reduced thus effecting a first color state. Upon a applying an AC electric field with frequency that is resonant with the vibrational mode of said charged heads cantilevered on said hairpin shaped molecule or spring said bond 287 may be mad to break hus yielding an open state 288. In said open state the leuco dye and reducing agent are no longer proximal and the leuco dye, being in a non-reduced state, effects a second color state. The system may be reversed by applying a DC electric field which serves to reproximate the leuco dye and reducing agent groups. Many molecules or microfabricated structures may serve as the normally open hairpin shaped molecule or spring. These may include oleic acid like molecules 289. Reducing agents may include sodium dithionite. We note that the system as discussed is bistable. We note also that energy may be stored in said hairpin shaped molecule or spring and as such said system may also function as a battery.

Referring to Figures 4I-K an alternative leucodye-reducing agent system may employ a polymer shown in Figure 4I in a natural state 293. When a DC electric field is applied said polymer assumes a linear shape 294 with leuco 286 and reducing agent 285 groups distal from each other. Upon application of either a reversing DC field or an AC electric field said polymer will tend to coil bringing into random contact said leuco and reducing groups forming a bond 287 with a corresponding color change. Said polymer serves to make said system bistable.

-13-

Referring to Figure 4L and M a similar system is possible but instead of a polymer leuco and reducing groups may be attached to oppositely charge microspheres directly by means of a bridge 296 which may be a
5 biotin-streptavidin bridge, polymer bridge or any other suitable bridge. As before application of a DC field cause leuco and reducing groups to become distal whereas application of a reverse DC field or AC field brings into random contact the leuco and reducing groups. A polymer
10 may be added to aid in the stability of the oxidized state.

Referring to Figures 5A-D and Figures 6A-B an entirely different principle may be employed in an electronically addressable contrast media ink. In these
15 systems the dielectrophoretic effect is employed in which a species of higher dielectric constant may be caused to move to a region of high electric field strength.

Referring to Figures 5A and 5B a non-colored dye solvent complex 315 which is stable when no field is
20 applied across electrode pair 150 may be caused to become dissociate into colored dye 300 and solvent 310 components by means of an electric field 170 acting differentially on the dielectric constant of said dye complex and said solvent complex as applied by electrode pair 150. It is
25 understood that the chemistries as discussed in the system of Figures 3C-D may readily be employed here and that said dye complex and said solvent complex need not themselves have substantially different dielectric constants but rather may be associated with other molecules or particles
30 such as microspheres with substantially different dielectric constants. Finally it is understood that a gel or polymer complex may be added to the contents of said microcapsule in order to effect a bistability.

-14-

Referring to Figures 5C-D stacked electrode pairs 150 and 160 may be employed to effect a high electric field region in a higher 170 or lower 180 plane thus causing a higher dielectric constant material such as one hemisphere of a bichromal microsphere 141 or one species of a mixture of colored species 147 to migrate to a higher or lower plane respectively and give the effect of differing color states. In such schemes materials 165 which may be dielectric materials or may be conducting materials may be employed to shape said electric fields.

Referring to Figures 6A-B, systems based on a frequency dependent dielectrophoretic effect are described. Such systems are addressed by means of applying a field of one frequency to produce a given color and applying a field of a different frequency to produce another color. Such a functionality allows for a rear addressed display.

Referring to Figure 6A, a microcapsule 120 encompasses an internal phase 184 which may be a material which has a frequency independent dielectric constant as shown in Plot 6C, curve 320 and which may have a first color B and material 182 which has a frequency dependent dielectric constant and a second color W. Said frequency dependent material may further have a high dielectric constant at low frequency and a smaller dielectric constant at higher frequency as shown in Figure 6C 322. Application of a low frequency AC field by means of electrodes 270 and 280 causes said material 182 to be attracted to the high field region proximal to the electrodes thus causing said microcapsule to appear as the color B when viewed from above. Conversely application of a high frequency AC field by means of electrodes 270 and 280 causes said material 184 to be attracted to the high

-15-

field region proximal the electrodes thus displacing material 182 and thus causing said microcapsule to appear as the color W when viewed from above. If B and W correspond to Black and White then a black and white display may be effected. A polymer material may be added to internal phase 184 to cause said system to be bistable in the field off condition. Alternatively stiction to the internal side wall of said capsule may cause bistability.

Referring to Figure 6A, material 182 and Figure 6C, this patent teaches the fabrication of a particle with an engineered frequency dependent dielectric constant. The means for fabricating this particle are depicted in Figures 1B, E and F. At low frequency such dipolar particles have sufficiently small mass that they may rotate in phase with said AC field thus effectively canceling said field and acting as a high dielectric constant material. At high frequency however the inertia of said particles is such that they cannot keep in phase with said AC field and thus fail to cancel said field and consequently have an effectively small dielectric constant.

Alternatively material 182 may be comprised of naturally occurring frequency dependent dielectric materials. Materials which obey a frequency dependence functionality similar to the artificially created dipole material discussed above and which follow curves similar to Figure 6C, curve 322 include materials such as Hevea rubber compound which has a dielectric constant of $K = 36$ at $f = 10^3$ Hz and $K = 9$ at $f = 10^6$ Hz, materials with ohmic loss as are known in Electromechanics of Particles by T.B. Jones incorporated herein by reference and macromolecules with permanent dipole moments.

Additionally material 182 may be a natural or

-16-

artificial cell material which has a dielectric constant frequency dependence as depicted in Figure 6D, curve 330 as are discussed in Electromechanics of Particles by T.B. Jones incorporated herein by reference. Such particles
5 are further suitable for fabrication of an electronically addressable contrast ink.

Referring to Figure 6B a system is depicted capable of effecting a color display. Microcapsule 120 contains a particle of a first dielectric constant, conductivity and
10 color 186, a particle of a second dielectric constant, conductivity and color and an internal phase of a third dielectric constant, conductivity and color 190. Referring to Plot 6E it is known in the art of electromechanics of particles that for particles with
15 ohmic loss (e.g. finite conductivity) that at low frequency the DC conductivity governs the dielectric constant whereas at high frequency the dielectric polarization governs the dielectric constant. Thus a particle with finite conductivity has a dielectric
20 constant K as a function of frequency f as in Plot 6 E, curve 338. A second particle of second color has a dielectric constant K as a function of frequency f as in Figure 6E, curve 340. Finally an internal phase with no conductivity has a frequency independent dielectric
25 constant K , curve 336. If an AC field of frequency f_1 is applied by means of electrodes 270 and 280, material 186 of color M will be attracted to the high field region proximal to said electrodes thus causing said microcapsule to appear as a mixture of the colors C and Y, due to the
30 other particle and internal phase respectively, when viewed from above. If an AC field of frequency f_2 is applied by means of electrodes 270 and 280 material 188 of color Y will be attracted to the high field region

-17-

proximal to said electrodes thus causing said microcapsule to appear as a mixture of the colors C and M when viewed from above. Finally if an AC field of frequency f_3 is applied by means of electrodes 270 and 280 internal phase
5 190 of color C will be attracted to the high field region proximal to said electrodes thus causing said microcapsule to appear as a mixture of the colors M and Y when viewed from above. If C M and Y correspond to Cyan, Magenta and Yellow a color display may be effected.

10 It is understood that many other combinations of particles with frequency dependent dielectric constants arising from the physical processes discussed above may be employed to effect a frequency dependent electronically addressable display.

15 In addition to the microencapsulated electronically addressable contrast media ink discussed in Figures 3-6, figures 7-9 depict other types of electronically active ink systems. In the prior art means are known for depositing metals or resistive materials in a binding
20 medium which may later be cured to form conducting or resistive traces. In the following description novel means are described for depositing semiconductive materials in a binder on a large class of substrate materials in one case and for depositing metals, resistive
25 materials or semiconductive materials outside of vacuum, in an arbitrary pattern, without the need for an etch step and on a large class of substrate materials in another case.

In one system a semiconductor ink 350 may be
30 fabricated by dispersing a semiconductor powder 355 in a suitable binder 356. Said semiconductive powder may be Si, Germanium or GaAs or other suitable semiconductor and may further be with n-type impurities such as phosphorous,

-18-

antimony or arsenic or p-type impurities such as boron, gallium, indium or aluminum or other suitable n or p type dopants as is known in the art of semiconductor fabrication. Said binder 356 may be a vinyl, plastic heat curable or UV curable material or other suitable binder as is known in the art of conducting inks. Said semiconductive ink 350 may be applied by printing techniques to form switch or logic structures. Said printing techniques may include a fluid delivery system 370 in which one or more inks 372, 374 may be printed in a desired pattern on to a substrate. Alternatively said ink system 350 may be printed by means of a screen process 377 in which an ink 380 is forced through a patterned aperture mask 378 onto a substrate 379 to form a desired pattern. Said ink pattern 360 when cured brings into proximity said semiconductive powder particles 355 to create a continuous percolated structure with semiconductive properties 365.

Referring to Figure 8 a system is depicted for causing a conductive or semiconductive trace 390 to be formed on substrate 388 in correspondence to an impinging light source 382 which may be steered by means of an optical beam steerer 384. The operation of said system is based upon a microcapsule 386 which contains a metal or semiconductive salt in solution. Upon being exposed to light 382 which may be a UV light said metal or semiconductive salt is reduced to a metal or semiconductor and said microcapsule is simultaneously burst causing deposition of a conductive or semiconductive trace.

Referring to Figure 9A an ink jet system for depositing metallic or semiconductive traces 410 is depicted. In this system a jet containing a metal or semiconductive salt 420 impinges upon a substrate 400 in conjunction with a jet containing a reducing agent 430.

-19-

As an example, to form a metallic trace Silver Nitrate (AgNO_3) may be used for jet 420 and a suitable aldehyde may be used for the reducing jet 430. Many other examples of chemistries suitable for the present system are known in the art of electroless plating. In all such examples it is understood that said jets are moveable and controllable such that an arbitrary trace may be printed.

Referring to Figure 9B a system which is similar to that of Figure 9A is depicted. In this case an electron beam 470 may be used instead of said reducing jet in order to bring about a reduction of a metal or semiconductive salt emanating from a jet 460. A ground plane 450 may be employed to ground said electron beam.

Referring to Figure 9C an ink jet system for depositing a metallic or semiconductive trace is depicted based on electroplating. In this system a metal or semiconductive salt in a jet 480 held at a potential V may be electroplated onto a substrate 410 thus forming a metallic or semiconductive trace.

Referring to Figure 9D means are known in the prior art for UV reduction of a metal salt from an ink jet head. In the present system a jet containing a metal or semiconductive salt 490 may be incident upon a substrate 400 in conjunction with a directed light beam 495 such that said metal or semiconductive salt is reduced into a conductive or semiconductive trace 410. Alternatively jet 490 may contain a photoconductive material and a metal salt which may be caused to be photoconductively electroplated onto surface 400 by means of application of light source 495 as is known in the field of photoconductive electroplating.

Referring to Figure 9E a system is depicted for a moveable deposition head 500 which contains a chamber 520

-20-

which may be filled with an inert gas via inlet 510 and which further contains thermal, sputtering, electron beam or other deposition means 530. Said moveable head 500 may print a metal, semiconductor, insulator, spin material or other material in an arbitrary pattern onto a large class of substrates 540. In some case such substrate 540 be cooled or chilled to prevent damage from said materials which may be at an elevated temperature.

Referring to Figure 10 said previously described electronically active ink systems and printing means may be applied to form switch or logic structures. As indicated in Figures 10A-B an NPN junction transistor may be fabricated consisting of a n-type emitter 950, a p-type base 954 and a n-type collector 952.

Alternatively a field effect transistor may be printed such as a metal oxide semiconductor. Such a transistor consists of a p-type material 970, an n-type material 966 an n-type inversion layer 968 an oxide layer 962 which acts as the gate a source lead 960 and a drain lead 964. It is readily understood that multiple layers of logic may be printed by using an appropriate insulating layer between said logic layers. Further three dimensional interconnects between different logic layers may be accomplished by means of vias in said insulating layers.

Referring to Figure 10D a printed solar cell may be fabricated by printing some or all of a metal contact layer 972, a p-type layer 974, an n type layer 976 and an insulating layer 978. Light 979 which impinges upon said structure generates a current as is known in the art of solar cells. Such printed solar cells may be useful in very thin compact and/or inexpensive structures where power is needed.

-21-

The ink systems and printing means discussed in the foregoing descriptions may be useful for the fabrication of a large class of electronically functional structures. Figures 11-14 depict a number of possible such structures
5 which may be fabricated.

Referring to Figure 11, an electronic display, similar to one described in a copending patent by Jacobson, is comprised of electronically addressable contrast media 640, address lines 610 and 620 and logic
10 elements 670 all or some of which may be fabricated with the ink systems and printing means as described in the foregoing descriptions.

Referring to Figure 12 an electrostatic motor which may form an analog clock or watch is depicted which
15 consists of printed conducting elements 720, 730, 740 and 760 which are printed onto substrate 700. Said elements, when caused to alternately switch between positive negative or neutral states by means of a logic control circuit 710 may cause an element 750 to be translated thus
20 forming a motor or actuator. In the device of Figure 12 some or all of said conducting elements and/or logic control elements may be printed using the ink systems and printing means described in the foregoing description.

Referring to Figure 13 a wrist watch 800 is depicted
25 in which the band 820 of said watch contains an electronically addressable display 830 in which some or all of the components of said display, including the electronically addressable contrast media, the address lines and/or the logic are fabricated by means of the ink
30 systems and printing means described in the foregoing description. Such a fabrication may be useful in terms of producing and inexpensive, easily manufacturable and thin display function. Control buttons 810 may serve to

-22-

control aspects of said display 830.

Referring to Figure 14, a spin computer is depicted in which dipoles 912 with dipole moment 914 are situated at the nodes of row 920 and column 930 address lines.

- 5 Such a computer works by means of initially addressing said dipoles to an initial condition by said address lines and then allowing dipole interactions to produce a final state of the system as a whole thus performing a calculation as is known in the art of Spin Ising models
10 and cellular automata. Said dipoles may consist of a dipolar microsphere 912 microencapsulated in a microcapsule 910 or may consist of another form of dipole and/or another means of encapsulation.

- 15 While this invention has been particularly shown and described with references to preferred embodiments thereof, it will be understood by those skilled in the art that various changes in form and details may be made therein without departing from the spirit and scope of the invention as defined by the appended claims.

-23-

CLAIMS

What is claimed is:

1. An electronically active ink comprising a microencapsulated system having an optical
5 reflectance which may be modulated by means of application of an electric field.
2. The ink of claim 1 in which said microencapsulated system is suitable for addressing by means of top and bottom electrodes.
- 10 3. The ink of claim 1 in which said microencapsulated system is suitable for addressing solely by means of bottom electrodes.
4. The ink of claim 1 in which said microencapsulated system is suitable for addressing by means of an AC
15 electric field which may be modulated at a first frequency to effect a first optical reflectance and at a second frequency to effect a second optical reflectance.
5. The ink of claim 4 in which said modulatable optical
20 reflectances correspond to modulatable colors.
6. Means of fabricating a bichromal particle employing electrostatically charged atomizers.
7. Means of fabricating a bichromal particle in which
25 differentially colored materials are electrostatically attracted to each other on a

-24-

spinning disk or double barrel nozzle.

8. Means of fabricating a particle with an implanted dipole employing an electrostatically charged atomizer, a spinning disk or a double barrel nozzle.
- 5 9. Means of fabricating a bichromal particle with an implanted dipole employing an electrostatically charged atomizer, a spinning disk or a double barrel nozzle.
- 10 10. The ink of claim 1 in which said microencapsulated system is based on a bichromal microsphere.
- 15 11. The ink of claim 10 in which said microencapsulated system is based on a bichromal microsphere fabricated by means of two materials brought together electrostatically by means of atomizers, spinning disk or double barrel nozzle.
- 20 12. The ink of claim 10 in which said microencapsulated system is based on a bichromal microsphere with implanted dipole.
- 25 13. The ink of claim 12 in which said microencapsulated system is based on a bichromal microsphere with implanted dipole fabricated with an electrostatically charged atomizer, a spinning disk or a double barrel nozzle.
14. The ink of claim 1 in which said microencapsulated system is based on an electrophoretic effect.

-25-

15. The ink of claim 1 in which said microencapsulated system is based on a dielectrophoretic effect.
16. An electronic display in which display elements employ a frequency dependent dielectrophoretic effect in which an AC electric field modulated at a first frequency effects a first optical reflectance and an AC electric field modulated at a second frequency effects a second optical reflectance.
17. The ink of claim 15 in which said dielectrophoretic effect is a frequency dependent dielectrophoretic effect.
18. The ink of claim 17 in which said frequency dependence is due to a particle with an implanted dipole.
19. The ink of claim 17 in which said frequency dependence is due to an elastomeric, ohmic loss, artificial or natural cell structure or natural dipole.
20. The ink of claim 18 in which said particle is fabricated by means of electrostatically charged atomizers, spinning disk or double barrel nozzle.
21. The ink of claim 1 in which said microencapsulated system is based on a two part dye and solvent or reducing and oxidizing system.
22. An electronic display in which display elements are comprised of a dye which is associated with a head of

-26-

one charge and a reducing, oxidizing or solvent agent associated with a head of opposite charge and which may be caused to effect a color of a first type upon application of an electric field of a first type and
5 a color of a second type upon application of a field of a second type.

23. The display of claim 22 further comprising a bistable molecule or spring configuration.
24. The display of claim 22 further comprising a polymer
10 or bridge molecule to which said dye and reducing, oxidizing or solvent and said charged head groups are attached.
25. The ink of claim 1 in which said microencapsulated system is based on a dye which is associated with a
15 charged head of one charge and a reducing, oxidizing or solvent agent associated with a charged head of opposite charge and which may be caused to effect a color of a first type upon application of an electric field of a first type and a color of a second type
20 upon application of a field of a second type.
26. The ink of claim 25 further comprising a bistable molecule or spring configuration.
27. The ink of claim 25 further comprising a polymer or
25 bridge molecule to which said dye and reducing, oxidizing or solvent and said charge head groups are attached.
28. The ink of claim 1 in which said microencapsulated

-27-

system is based on an electroluminescent system coupled to an electronically active dye system.

29. The ink of claim 1 in which said microencapsulated system is based on a bistable liquid crystal system.
- 5 30. The ink of claim 1 in which said microencapsulated system is individually microencapsulated.
31. The ink of claim 1 in which said microencapsulated system is matrix microencapsulated.
- 10 32. An electronically active ink comprising a microencapsulated spin system.
33. An electronically active ink comprised of a semiconductive material in a binder.
- 15 34. A printing means for printing a conducting or semiconducting trace by means of causing a light source to be scanned such that a substrate containing a microencapsulated salt is reduced and burst in areas where said light source impinges thus forming said conducting or semiconducting trace.
- 20 35. A printing means for printing a conducting or semiconducting trace by means of moveable jets in which one such jet contains a salt and another such jet contains a reducing agent.
- 25 36. A printing means for printing a conducting or semiconducting trace by means of a moveable jet and electron beam in which a salt from said jet is

-28-

reduced by said electron beam.

37. A printing means for printing a conducting or semiconducting trace by means of a moveable jet containing a salt in an electroplating configuration.
- 5 38. A printing means for printing a conducting, semiconducting, insulating or resistive trace by means of a moveable head further comprising a sputter, thermal evaporation or electron beam element and a local vacuum or inert gas provision.
- 10 39. A semiconductor which may be a diode, transistor or opto-electronic structure produced by means of a printing process.
40. An electronic device comprised of multiple layers of said semiconductor devices of Claim 39.
- 15 41. An electronic device of claim 40 which includes an insulating layer which further may have vias and three dimensional interconnects.
42. An electronically addressable display in which some or all of address lines, electronically addressable contrast media, logic or power elements are
20 fabricated by means of a printing process.
43. An electronically addressable display in which some or all of address lines, electronically addressable contrast media, logic or power elements employ an
25 electronically active ink.

-29-

44. An electrostatic motor or actuator in which some or all of address lines, logic or power elements are fabricated by means of a printing process.
- 5 45. A wristwatch band comprising an electronically addressable display in which some or all of address lines, electronically addressable contrast media, logic or power elements are fabricated by means of a printing process.
- 10 46. A wristwatch band comprising an electronically addressable display in which some or all of address lines, electronically addressable contrast media, logic or power elements employ an electronically active ink.
- 15 47. A spin computer in which some or all of address lines, electronically addressable spin media, logic or power elements are fabricated by means of a printing process.
- 20 48. A spin computer in which some or all of address lines, electronically addressable spin media, logic or power elements employ an electronically active ink.

1/25

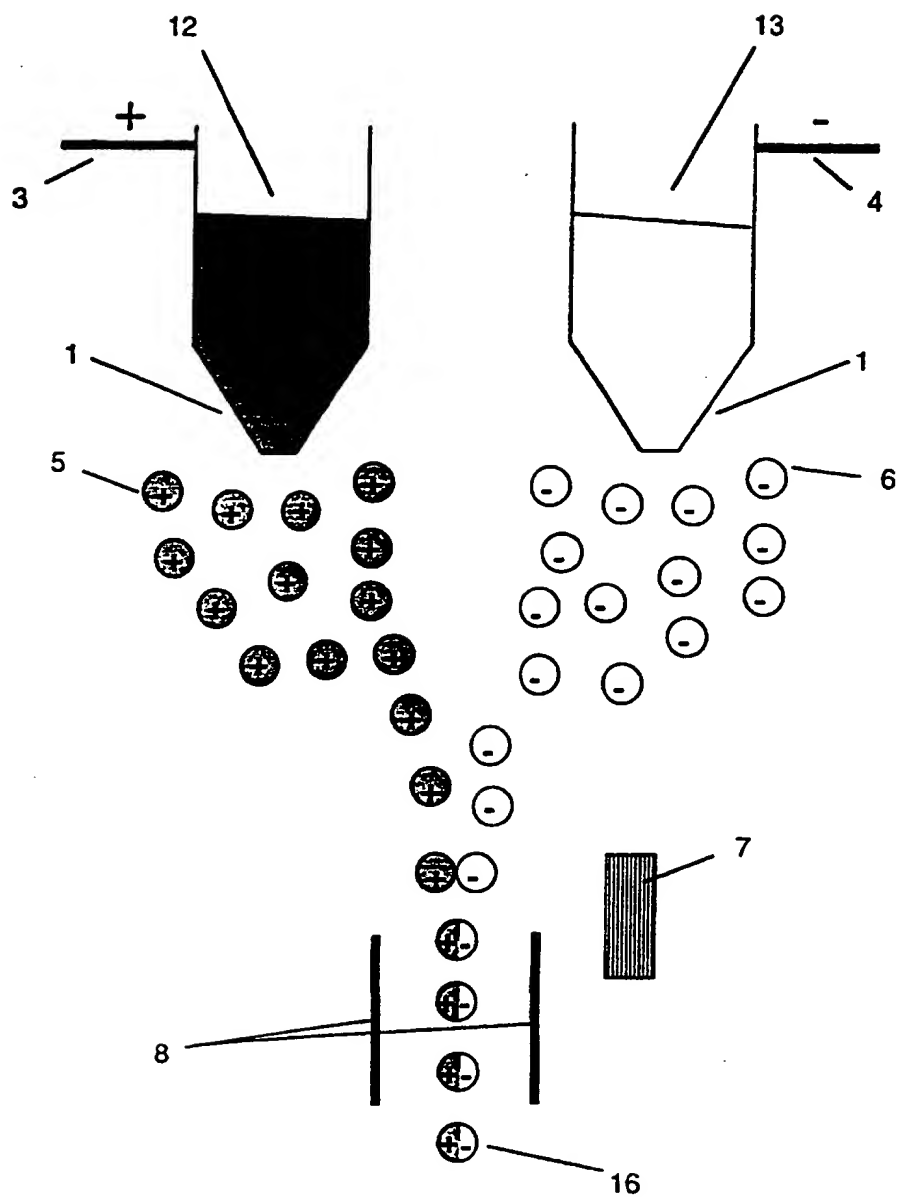


FIG 1 A

SUBSTITUTE SHEET (RULE 26)

2/25

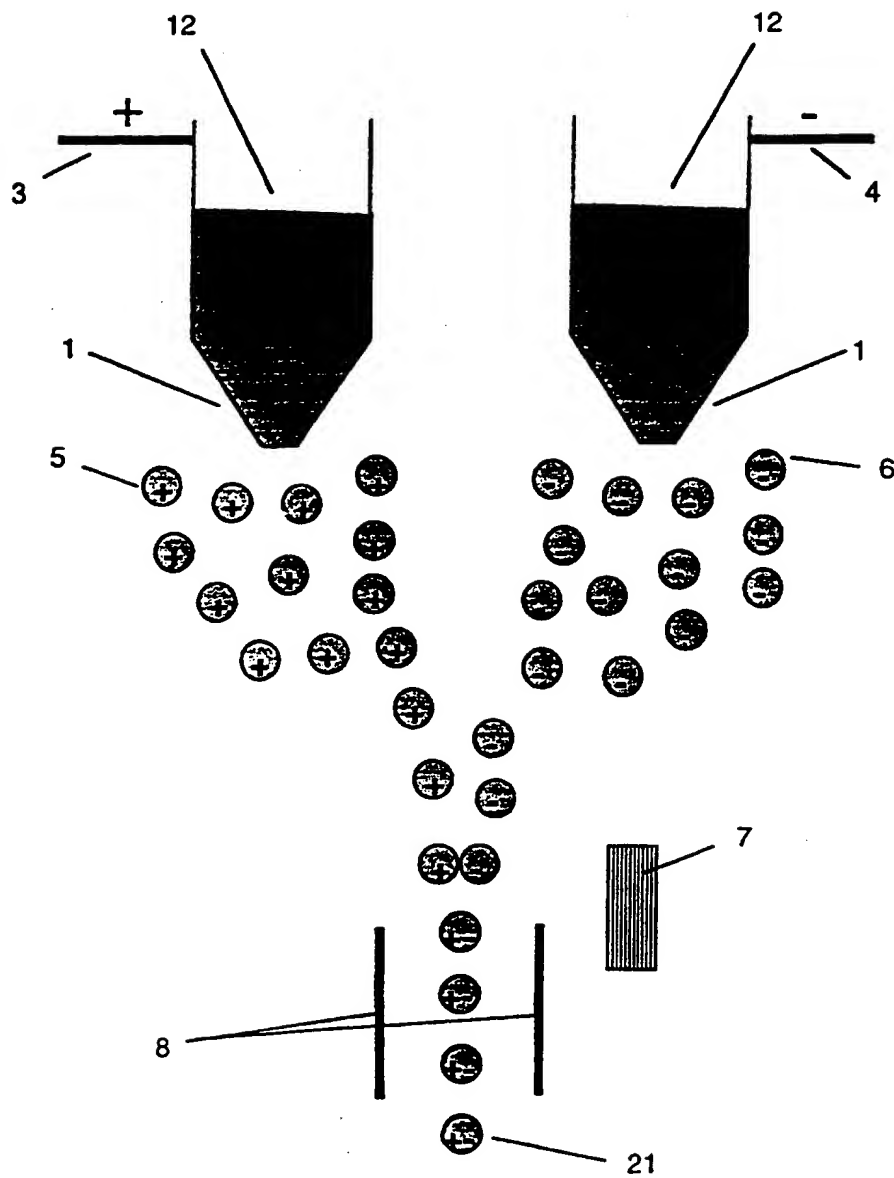


FIG 1 B

SUBSTITUTE SHEET (RULE 26)

3/25

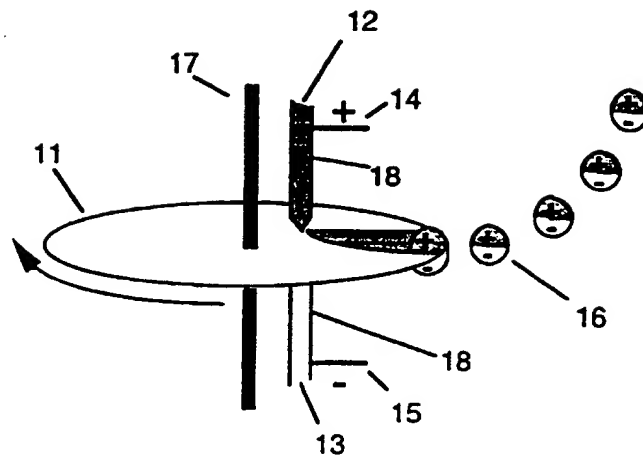


FIG 1 C

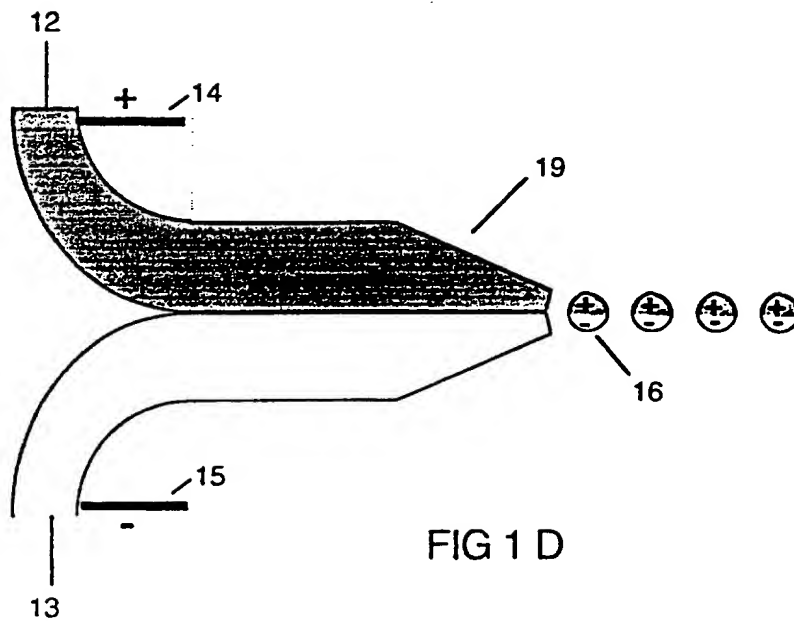


FIG 1 D

4/25

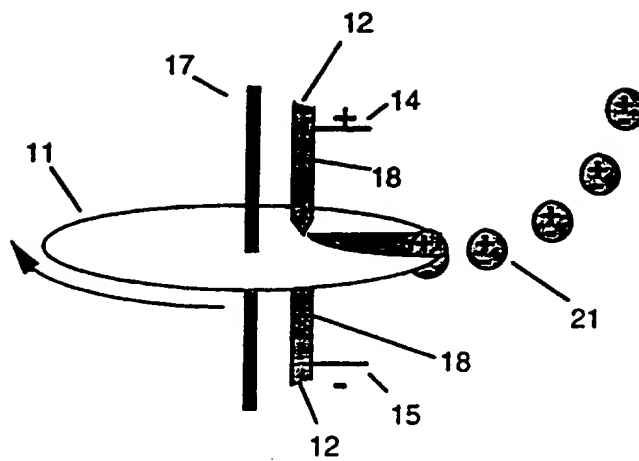


FIG 1 E

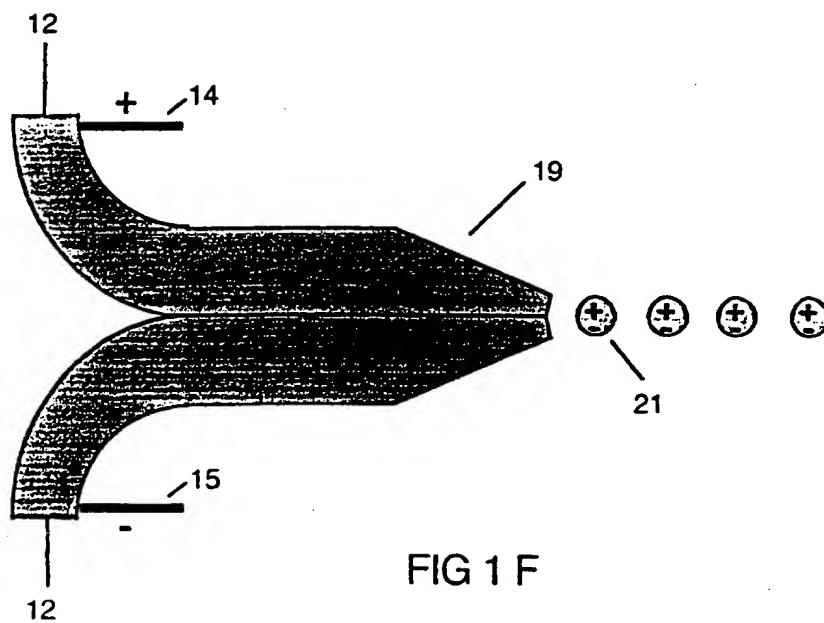


FIG 1 F

5/25

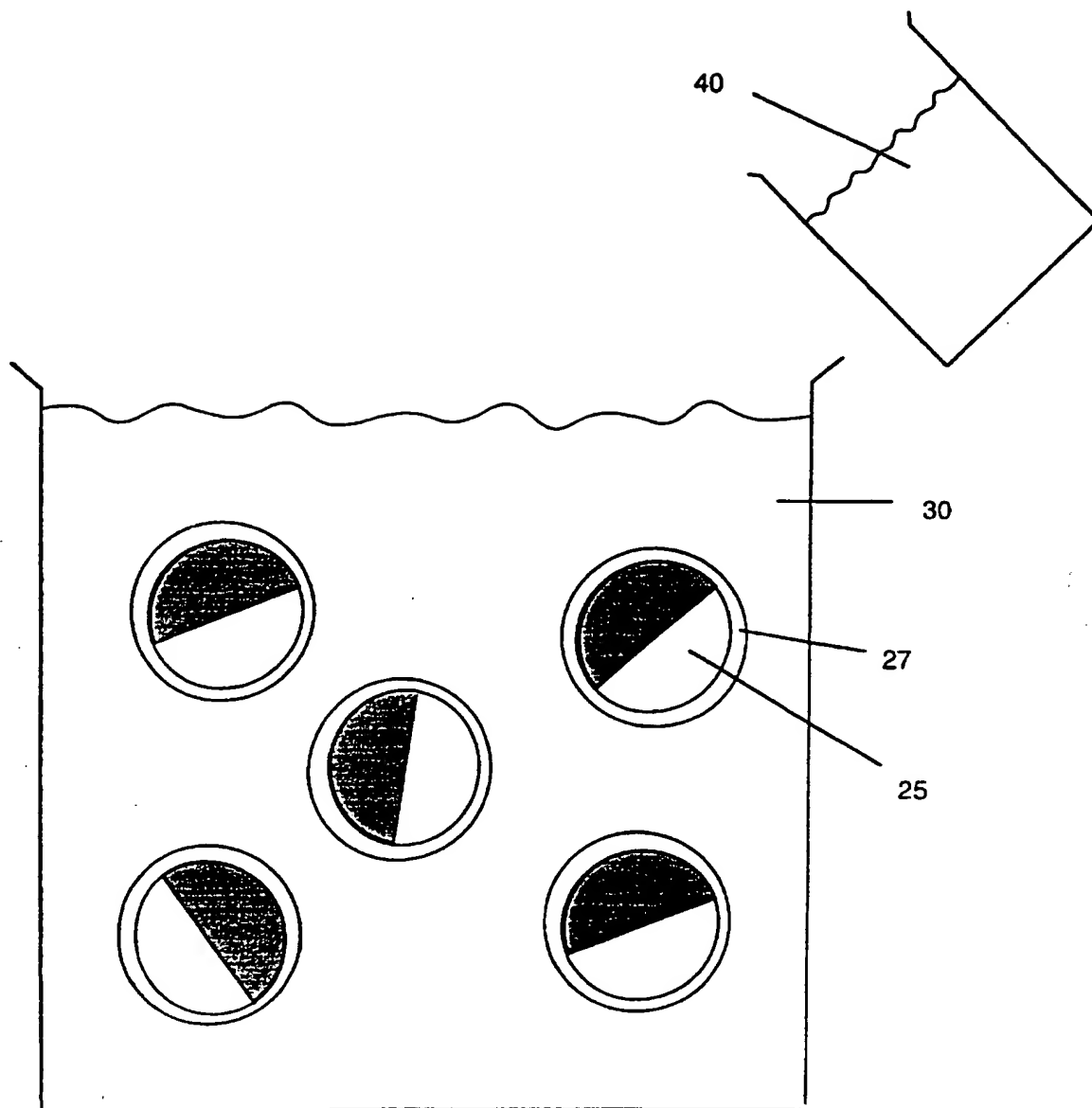


FIG 2 A

6/25

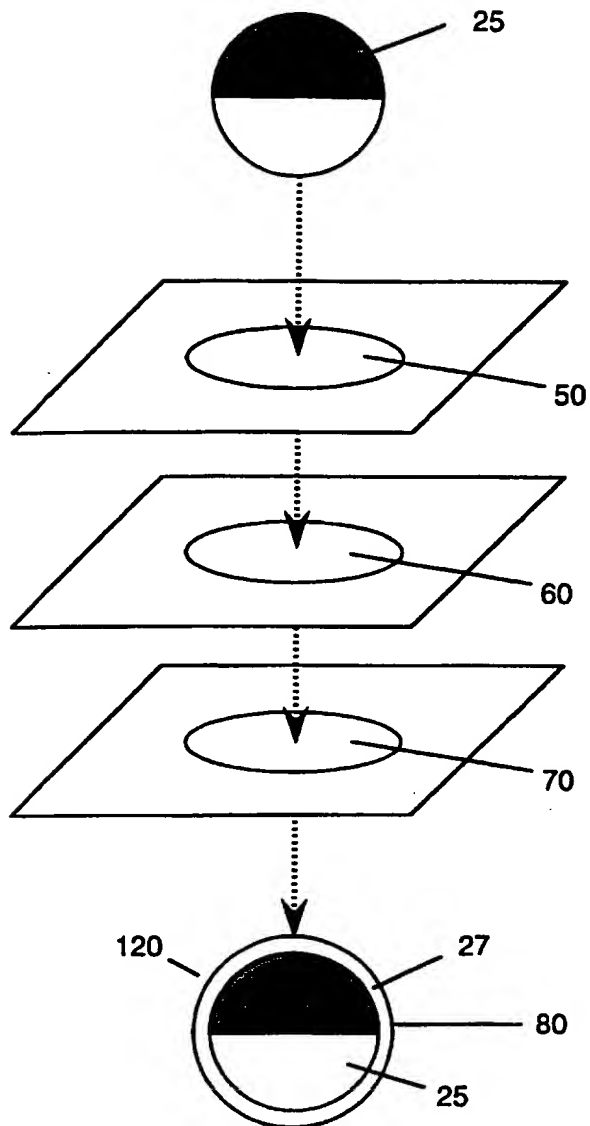


FIG 2 B

SUBSTITUTE SHEET (RULE 26)

7/25

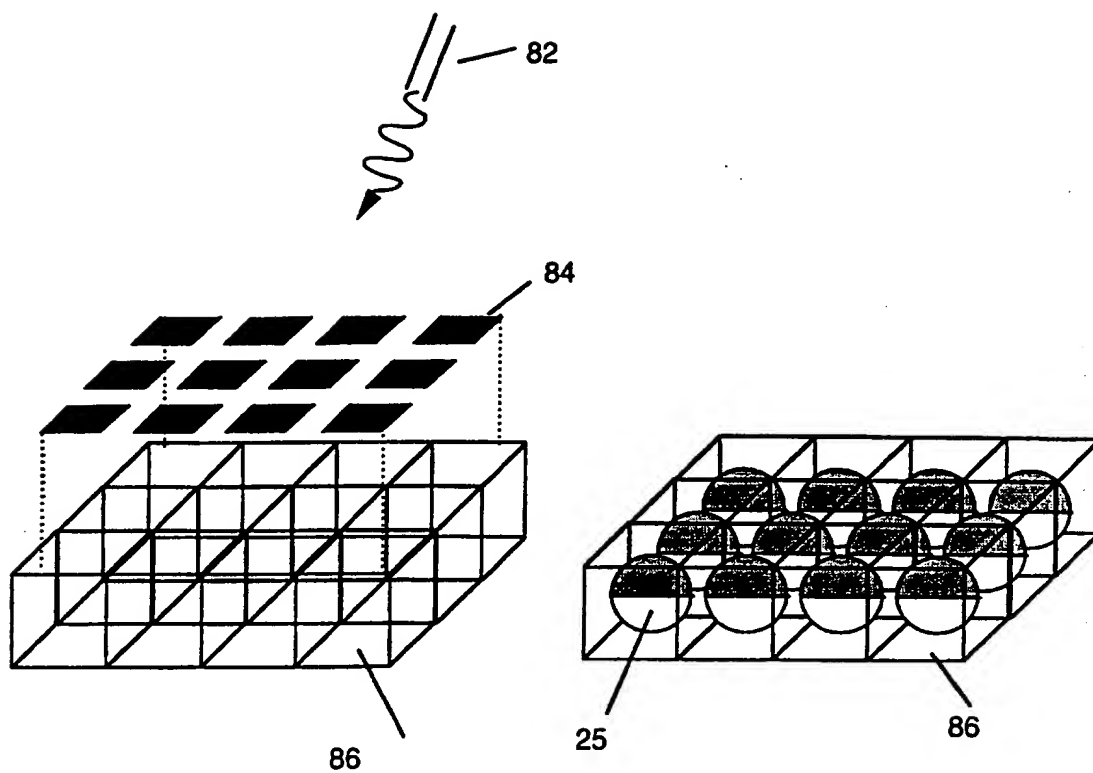
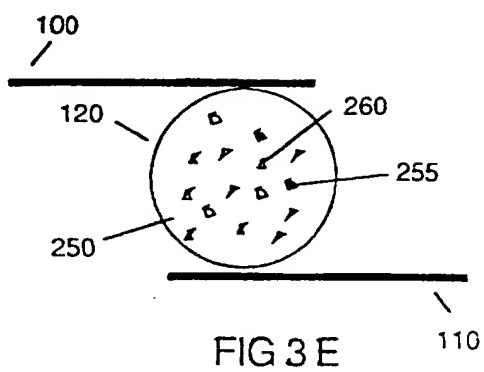
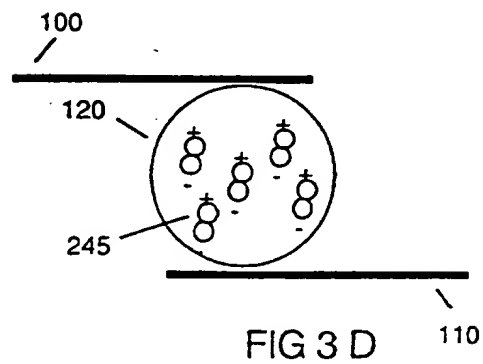
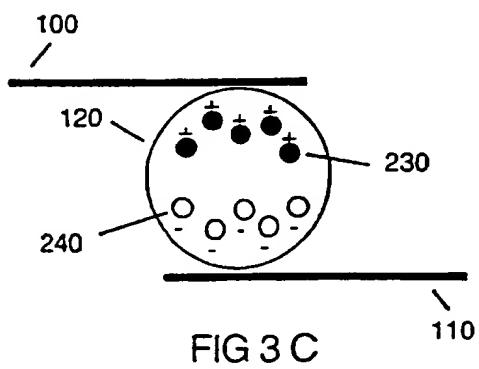
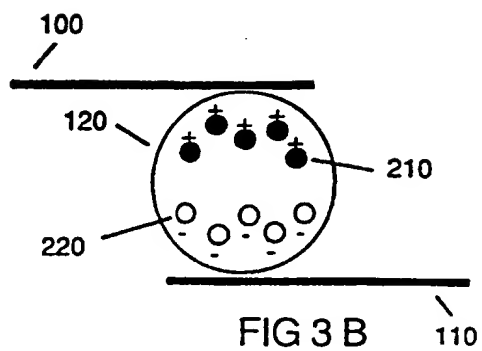
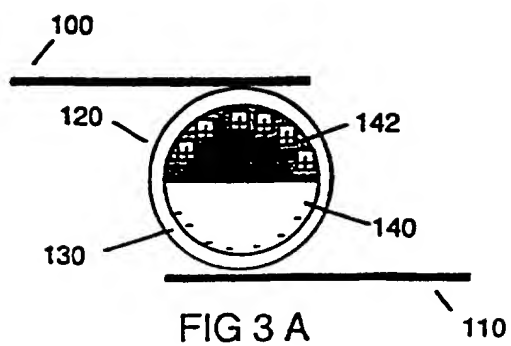


FIG 2 C

SUBSTITUTE SHEET (RULE 26)

8/25



9/25

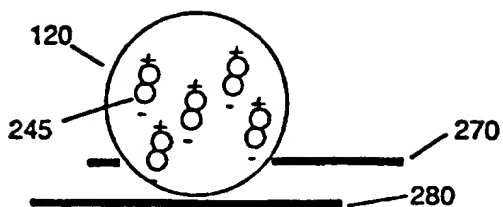


FIG 4 A

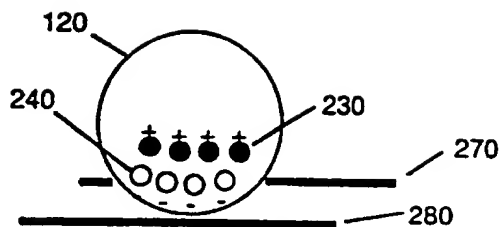


FIG 4 B

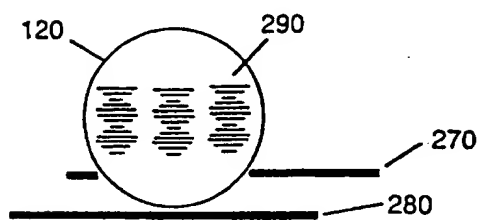


FIG 4 C

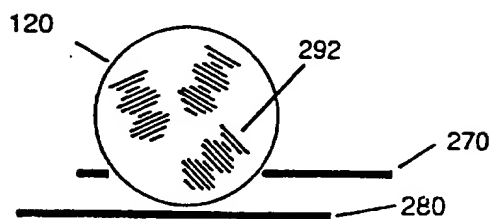


FIG 4 D

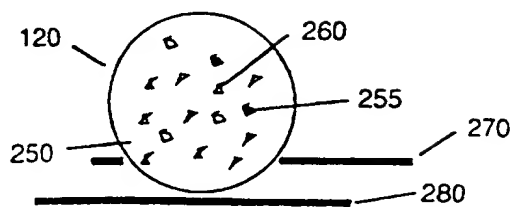


FIG 4 E

10/25

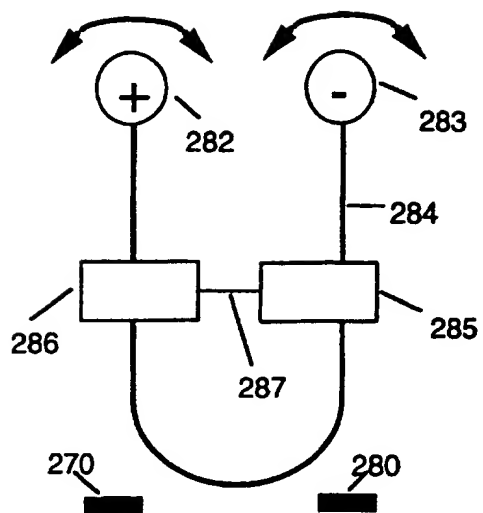


FIG 4 F

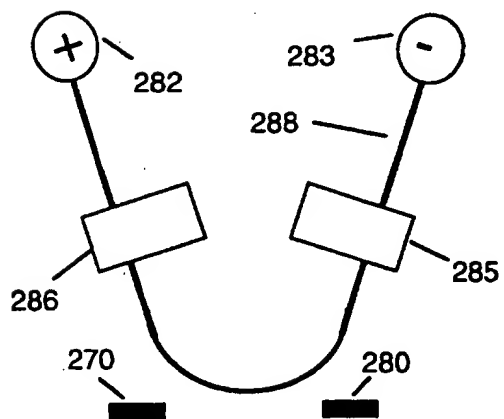


FIG 4 G

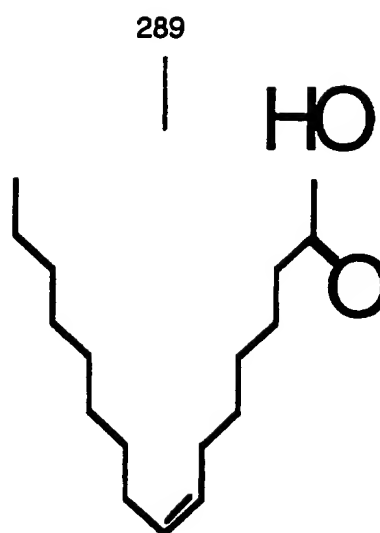


FIG 4 H

11/25

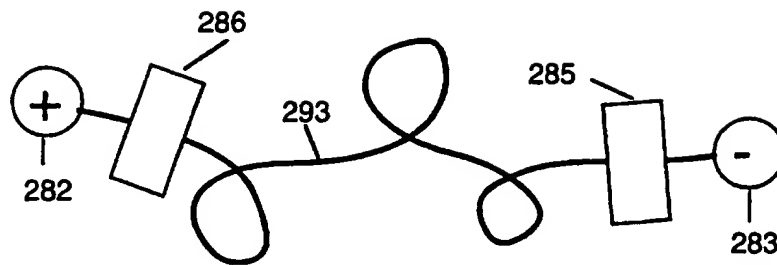


FIG 4 I

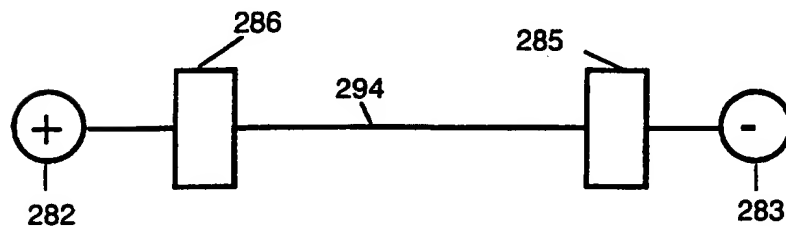


FIG 4 J

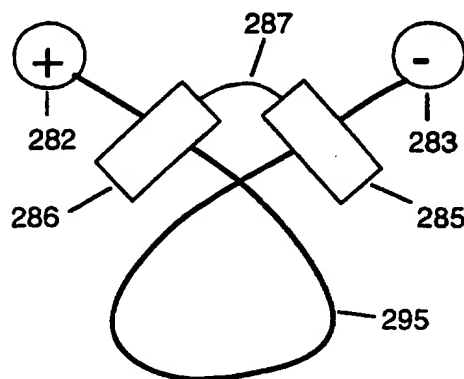


FIG 4 K

12/25

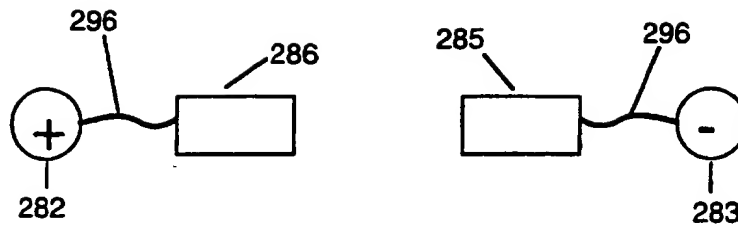


FIG 4 L

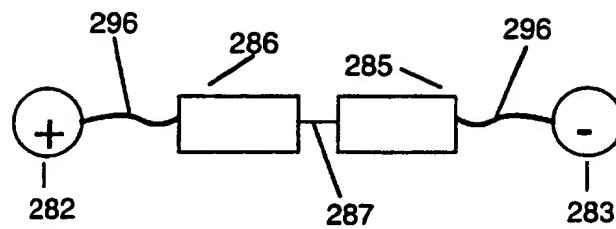


FIG 4 M

13/25

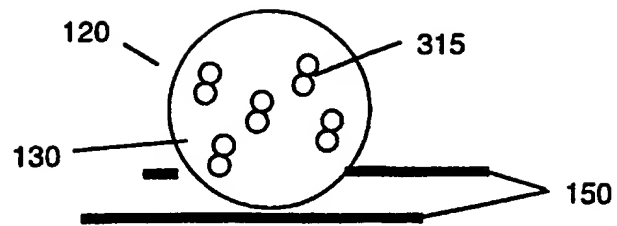


FIG 5 A

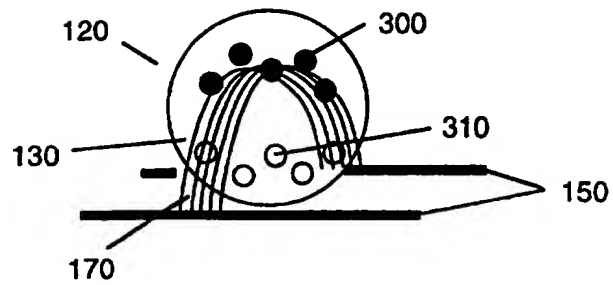


FIG 5 B

14/25

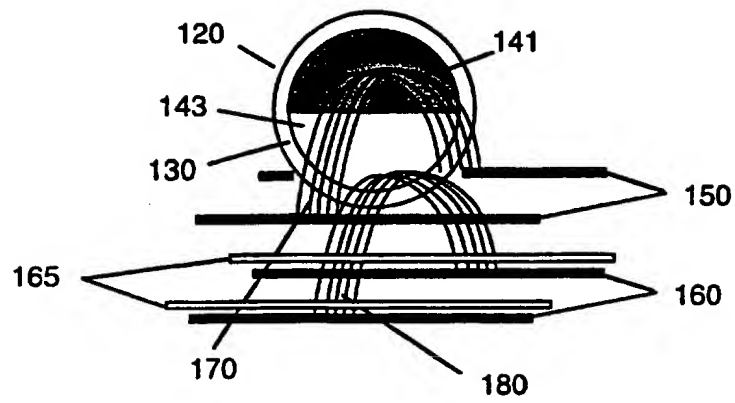


FIG 5 C

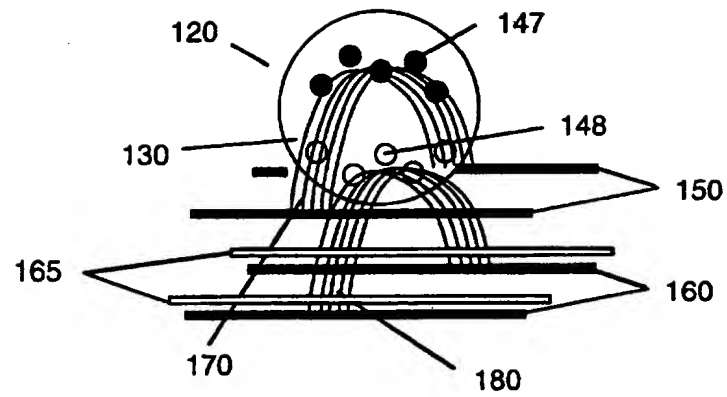


FIG 5 D

15/25

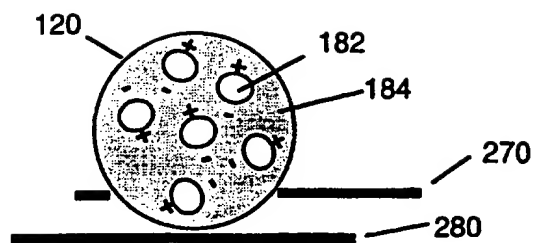


FIG 6 A

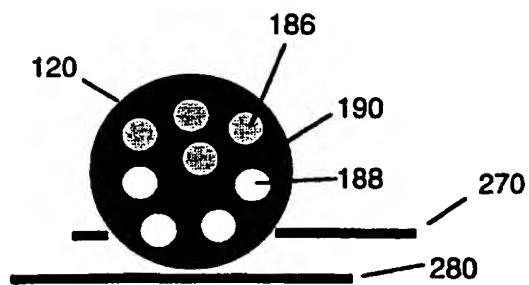


FIG 6 B

16/25

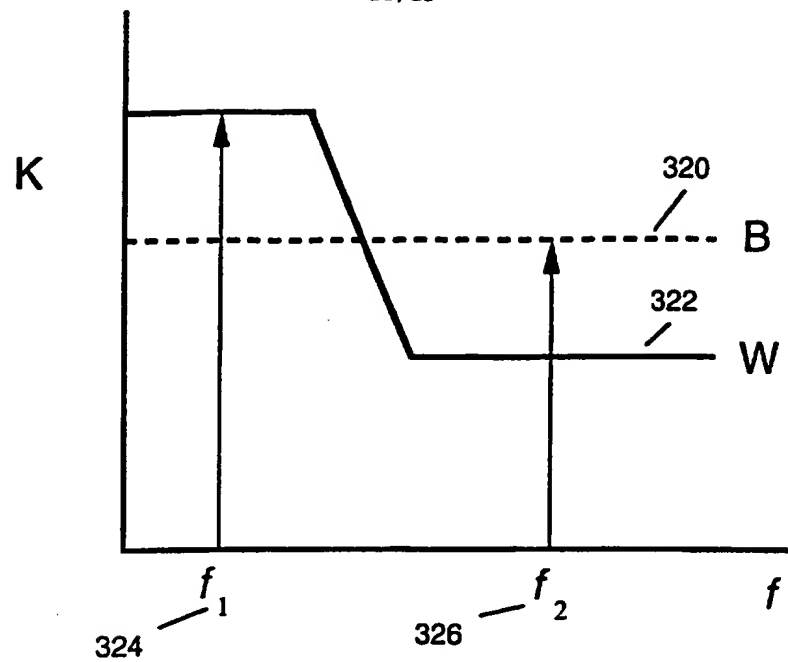


FIG 6 C

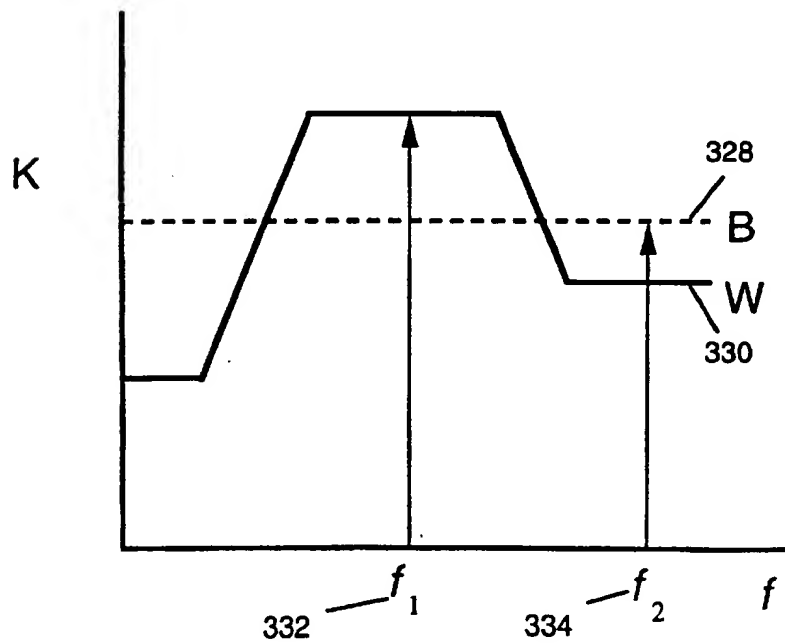


FIG 6 D

17/25

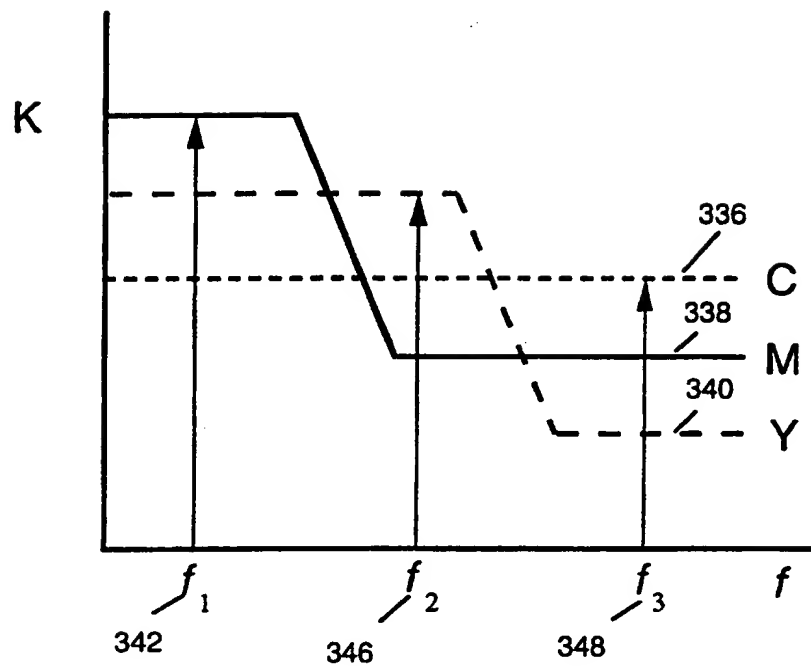


FIG 6 E

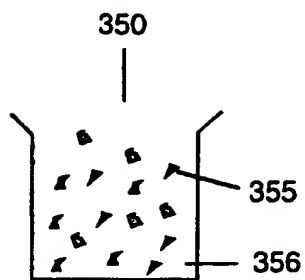


FIG 7 A

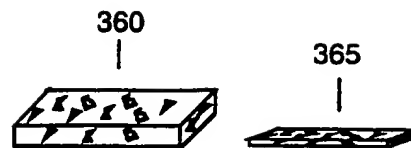


FIG 7 D

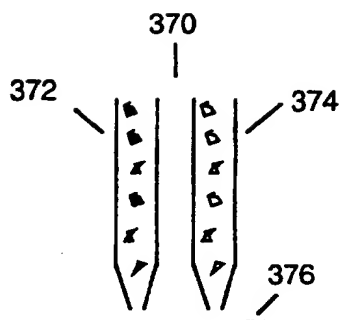


FIG 7 B

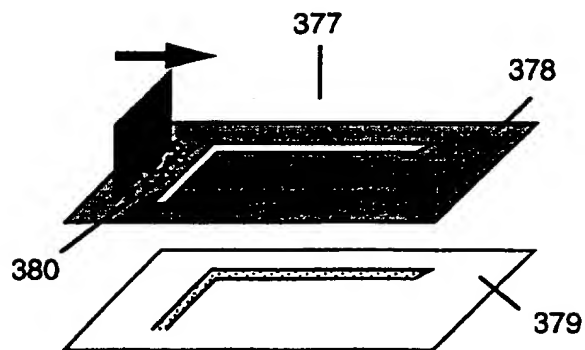


FIG 7 C

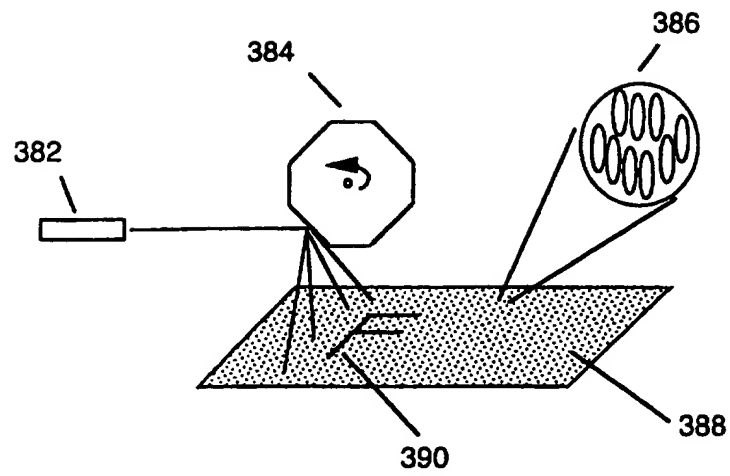


FIG 8

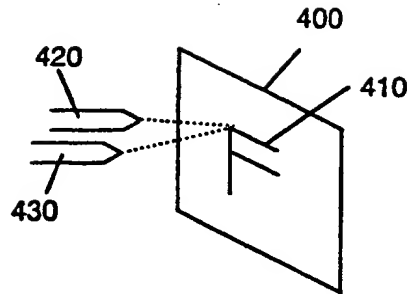


FIG 9 A

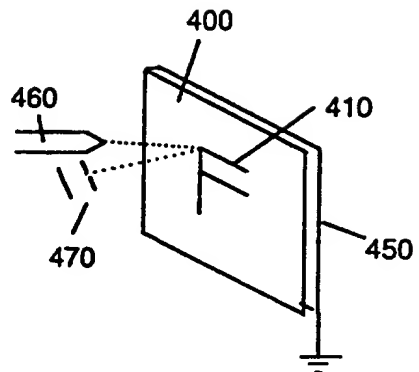


FIG 9 B

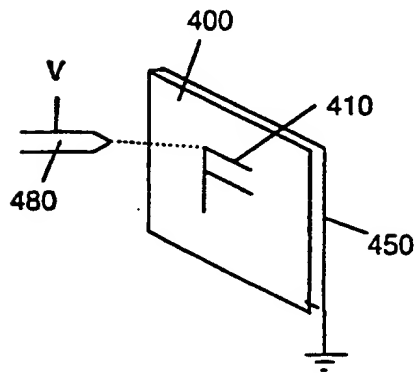


FIG 9 C

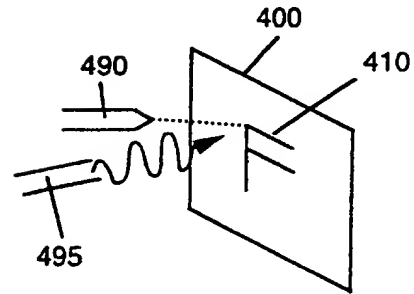


FIG 9 D

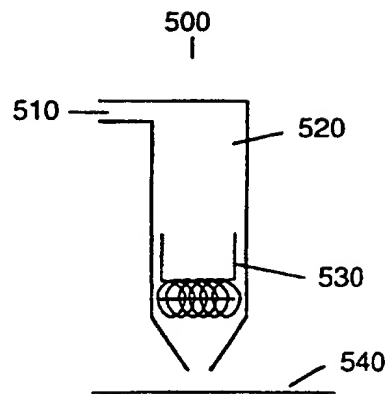


FIG 9 E

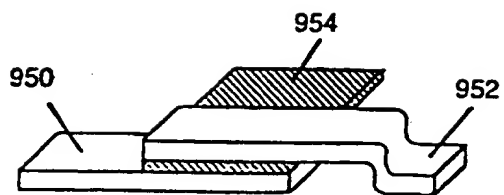


FIG 10 A

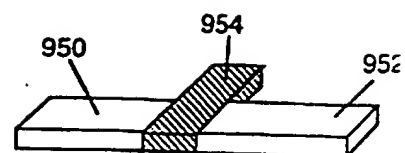


FIG 10 B

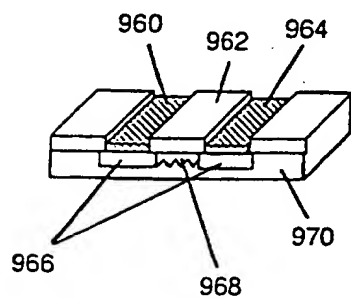


FIG 10 C

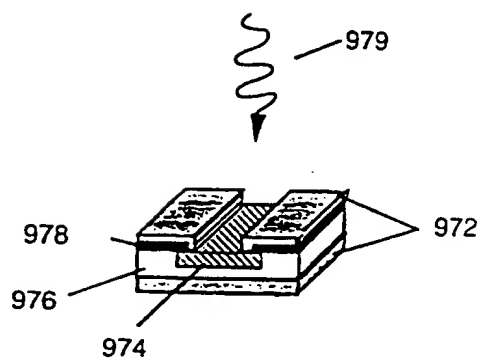


FIG 10 D

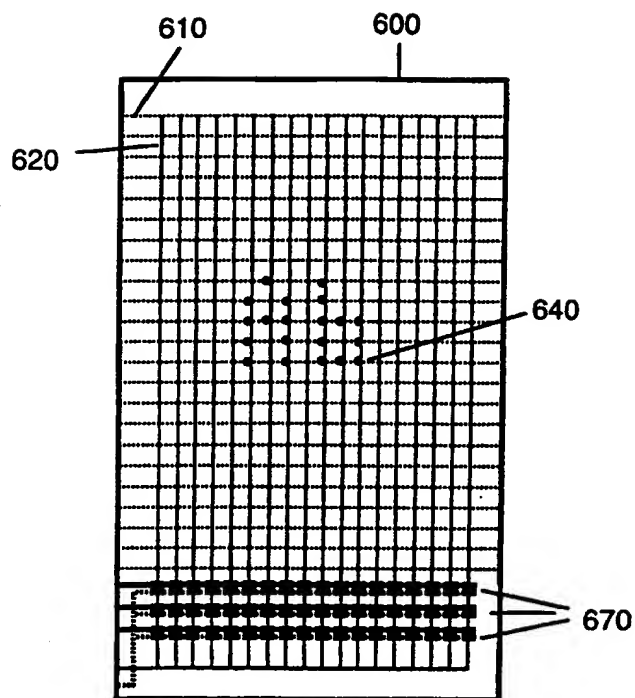


FIG 11

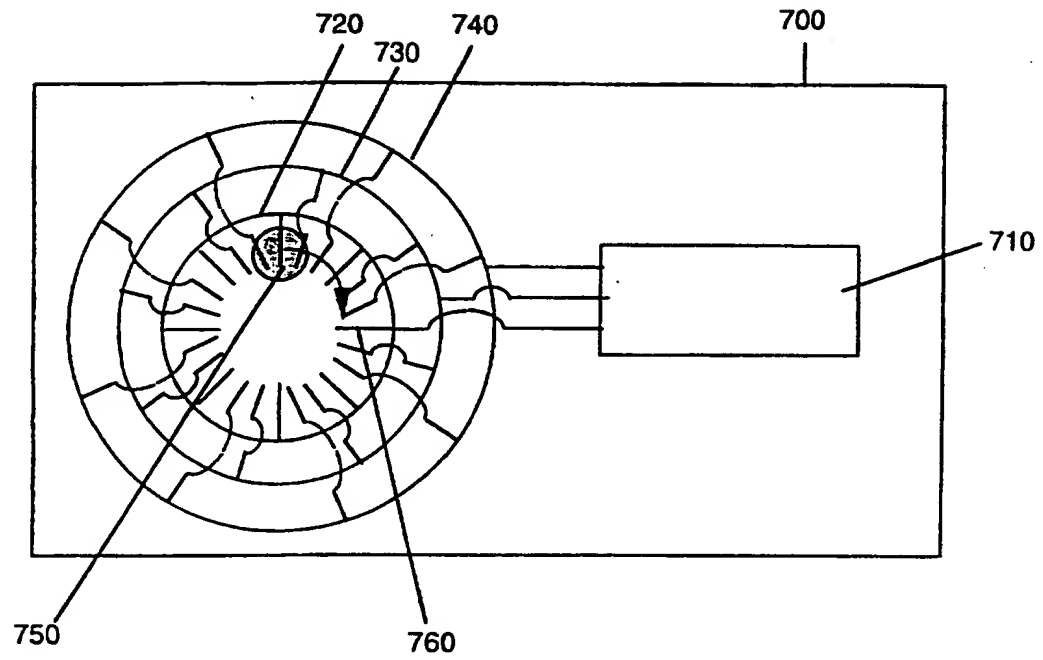


FIG 12

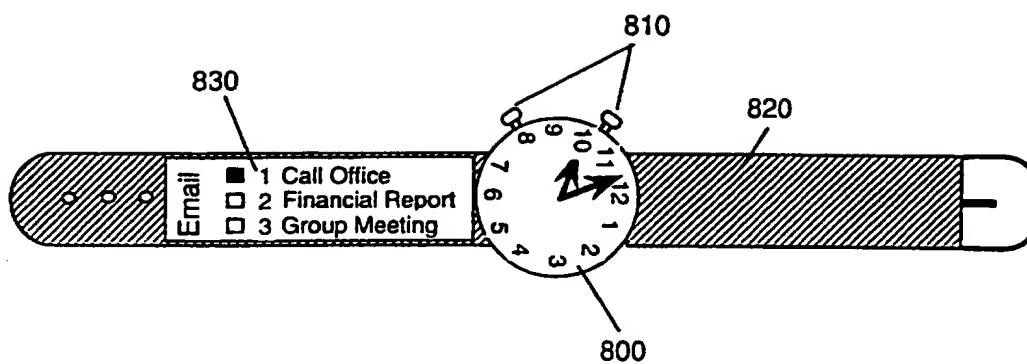


FIG 13

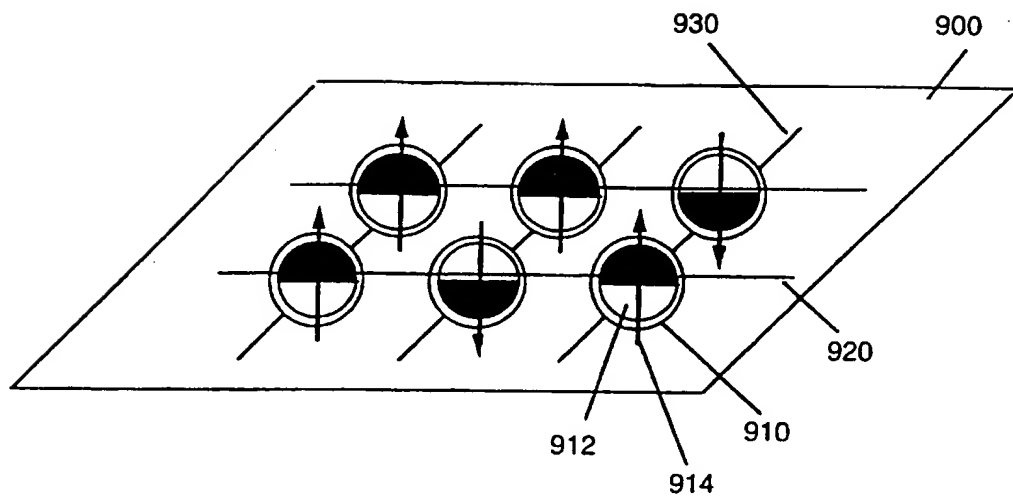


FIG 14

International Application No
PCT/US 96/13469

PCT/US 96/13469

A. CLASSIFICATION OF SUBJECT MATTER		CLASSIFICATION		CLASSIFICATION	
IPC 6	G02F1/133	B41J2/01	B29C67/00	G09F9/00	G04B47/00
	G09F9/37				

B. FIELDS SEARCHED

IPC 6 G02F B41J B29C G09F G04B

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 012, no. 100 (P-683), 2 April 1988 & JP 62 231930 A (STANLEY ELECTRIC CO LTD), 12 October 1987, see abstract	1-5, 29-31
Y	---	6-11
X	PATENT ABSTRACTS OF JAPAN vol. 011, no. 252 (P-605), 15 August 1987 & JP 62 058222 A (RICOH CO LTD), 13 March 1987, see abstract	1-5, 29-31
X	---	
X	EP 0 721 176 A (XEROX CORPORATION) 10 July 1996 see the whole document ---	1,2

	-/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

- * "A" document defining the general state of the art which is not considered to be of particular relevance
- * "E" earlier document but published on or after the international filing date
- * "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- * "O" document referring to an oral disclosure, use, exhibition or other means
- * "P" document published prior to the international filing date but later than the priority date claimed

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

*& document member of the same patent family

11 April 1997

27.06.97

Authorized officer _____

MEULEMANS, J

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 96/13469

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 508 068 A (NAKANO) 16 April 1996 see the whole document ---	1,29
Y	PROCEEDINGS OF THE SID, vol. 23, no. 4, 1 January 1982, pages 249-253, XP000561201 SAITOH M ET AL: "A NEWLY DEVELOPED ELECTRICAL TWISTING BALL DISPLAY" see the whole document ---	10
Y	EP 0 540 281 A (XEROX CORPORATION) 5 May 1993 see the whole document ---	8,9,11
Y	EP 0 281 204 A (DOTT. BONAPACE & C.S.P.A) 7 September 1988 see the whole document ---	6-9,11
A	EP 0 443 571 A (UBE INDUSTRIES, LTD.) 28 August 1991 see the whole document ---	1
A	US 5 398 131 A (HALL ET AL.) 14 March 1995 see the whole document ---	1,29
A	EP 0 268 877 A (MANCHESTER R & D PARTNERSHIP) 1 June 1988 see the whole document ---	1
A	PATENT ABSTRACTS OF JAPAN vol. 018, no. 349 (P-1763), 30 June 1994 & JP 06 089081 A (SONY TEKTRONIX CORP), 29 March 1994, see abstract ---	4
A	JOURNAL OF APPLIED PHYSICS, vol. 65, no. 12, 15 June 1989, pages 5043-5050, XP000072423 VAZ N A ET AL: "DUAL FREQUENCY ADDRESSING OF POLYMER-DISPERSED LIQUID-CRYSTAL FILMS" see the whole document ---	4
A	US 4 143 103 A (SHERIDON) 6 March 1979 see the whole document ---	1,6,10
A	EP 0 186 710 A (NISSHA PRINTING KK) 9 July 1986 see the whole document ---	1,29
A	US 4 643 528 A (BELL, JR.) 17 February 1987 see the whole document -----	1,29

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 96/13469

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

Group 1 claims 1-13, 29-31
Group 2 claims 14-20
Group 3 claims 21-28
Group 4 claims 32-48

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

1-13 & 29-31

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 96/13469

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 721176 A	10-07-96	US 5604027 A JP 8234686 A	18-02-97 13-09-96
US 5508068 A	16-04-96	DE 69021950 D DE 69021950 T EP 0404639 A JP 1829766 C JP 3103489 A US 5198148 A JP 3129320 A JP 7086609 B	05-10-95 28-03-96 27-12-90 15-03-94 30-04-91 30-03-93 03-06-91 20-09-95
EP 540281 A	05-05-93	DE 69211948 D DE 69211948 T JP 5279486 A US 5344594 A	08-08-96 28-11-96 26-10-93 06-09-94
EP 281204 A	07-09-88	JP 63252542 A	19-10-88
EP 443571 A	28-08-91	JP 4036720 A JP 3267917 A	06-02-92 28-11-91
US 5398131 A	14-03-95	NONE	
EP 268877 A	01-06-88	US 4435047 A AU 567868 B AU 1201583 A BR 8207867 A CA 1186502 A EP 0088126 A GB 2128626 A,B HK 42789 A HK 78191 A JP 6051284 A JP 4305620 A JP 7009512 B JP 3052843 B JP 58501631 A KR 9700345 B SU 1620056 A	06-03-84 10-12-87 06-09-84 30-08-83 07-05-85 14-09-83 02-05-84 09-06-89 11-10-91 25-02-94 28-10-92 01-02-95 13-08-91 29-09-83 08-01-97 07-01-91

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 96/13469

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 268877 A		WO 8301016 A	31-03-83
		US 4884873 A	05-12-89
		US 5082351 A	21-01-92
		US 4606611 A	19-08-86
		US 4616903 A	14-10-86
		US 4707080 A	17-11-87
		US 5089904 A	18-02-92
		US 4605284 A	12-08-86
		US 4579423 A	01-04-86
		US 4810063 A	07-03-89
		US 4844596 A	04-07-89

US 4143103 A	06-03-79	CA 1081834 A	15-07-80
		GB 1578460 A	05-11-80

EP 186710 A	09-07-86	JP 61004020 A	09-01-86
		DE 3586742 A	12-11-92
		WO 8600424 A	16-01-86
		US 4776675 A	11-10-88

US 4643528 A	17-02-87	CA 1261049 A	26-09-89
		GB 2172606 A,B	24-09-86
		JP 7009511 B	01-02-95
		JP 61269120 A	28-11-86
